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Solvent Swelling Influences the Electrochemical Behavior and Stability of Thin Films of Nitrated Poly(styrene)

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Abstract - The electrochemical behavior and stability of thin films of poly(nitrostyrene) (PNS) and a partially dinitrated derivative of PNS (PDNS) have been examined in acetonitrile. Qualitative information regarding the extent of solvent swelling of these polyelectrolyte films in nonaqueous solvents is obtained using the electrochemical quartz crystal microbalance (EQCM) technique, both by measuring the frequency changes due to solvent swelling and by measuring the conductance (impedance) spectra of the quartz crystal/polymer film composite resonator in the different oxidation states. Extensive solvent swelling as a function of the number of reductive scans is correlated with instability of the films toward dissolution or delamination and with subtle changes in electrochemical behavior. The effectiveness of thermal pretreatments (which presumably induce crosslinks of some type) for enhancing film stability by slowing the rate of swelling is examined. For certain types of films, it is shown that the transport processes which serve to achieve electroneutrality at high scan rates may occur on a different time scale (i.e. faster) than those which serve to attain thermodynamic equilibrium. The implication is that transient, non-equilibrium states may be prepared during switching whose composition is not necessarily that dictated by the equilibrium state, and that manipulation of these transient states to achieve faster switching rates may be done independently of equilibrium considerations, at least in some cases.



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Introduction

The importance of swelling processes in contributing to the types of behavior observed in the electrochemistry of thin polymer films has been recognized for some time (1). Swelling due to incorporation of solvent and ionic or neutral ion aggregate species from the supporting electrolyte can influence the activities of the redox groups in such films, thereby providing a possible origin for the non-Nernstian responses frequently seen in such systems (2,3). Swelling can also cause changes in the kinetics of redox processes by plasticizing the films (4) (which can change the glass transition temperature, T_g , and, therefore, the collision frequencies of the pendent redox groups), by changing the free volume and/or viscosity within the film, which can cause changes in the mobilities of incorporated species (4), and by changing the mean separation distance between the redox groups, and therefore, the efficiency of the electron hopping processes by which charge propagates through such films (1,5). Thus, both the kinetic and thermodynamic processes which dictate the overall electrochemical behavior of thin polymer films can be profoundly influenced by changes in the state of swelling.

Various methods have been applied to the study of swelling in thin, redox polymer films. These include profilimetry (6), ellipsometry (7-11), and the electrochemical quartz crystal microbalance (2,3,12-14). The first is not widely applicable due to the inherent frailty of many thin film systems. Ellipsometry provides very accurate, and extremely useful measurements of thickness, but suffers in the determination of compositions because of a lack of information about the partial molar volumes of the various species within the film. The EQCM, on the other hand, provides information complementary to that obtained from an ellipsometric experiment, in that mass measurements can give compositions but not thicknesses. As an aside, it would seem that the combination of these two techniques would provide an especially powerful tool with which to more fully describe thin film systems.

In this report the EQCM is used to study swelling processes in thin films of poly(nitrostyrene) (PNS) and a partially dinitrated derivative (PDNS) as a function of length of exposure and amount of redox cycling in acetonitrile. PNS was chosen for study due to

previous reports of its relative stability in nonaqueous solvents (15,16). In addition, since it functions as a cation exchange material in its reduced form, it is a good system with which to compare the behavior of poly(vinylferrocene) (which is an anion exchanger in its oxidized form), a polymer which has been previously investigated using both EQCM (3,14,17) and ellipsometry (7,8) in aqueous and nonaqueous solutions.

Experimental

PNS was prepared using a procedure similar to that described by Zenftman (18), in which poly(styrene) is nitrated using fuming nitric acid. Granular poly(styrene) (Aldrich) of molecular weight of $430,165 \text{ g mol}^{-1}$ was used. Elemental analysis (Desert Analytics, Tucson, Arizona) of the polymeric product gave: 61.15 % C, 4.74 % H, 9.58 % N to be compared with the calculated values of 64.42 % C, 4.71 % H, 9.40 % N. The partially dinitrated derivative (PDNS) was obtained from Polysciences under the label of poly(nitrostyrene) (lot #54483). Elemental analysis of a typical sample was: 55.97 % C, 3.73 % H, 11.97 % N. This indicates that 45% of the pendent phenyl groups have been dinitrated.

Burdick and Jackson spectral grade acetonitrile (ACN) was stored over 3A molecular sieves which were activated at 180°C for 48 hours prior to use. This solvent was used for most of the experiments. In some other cases, Kodak spectral grade acetonitrile was used. This was distilled twice, first from CaH_2 , then from P_2O_5 , and stored over 3A molecular sieves. For the casting of films, PNS and PDNS were dissolved in dimethyl formamide (DMF). Tetraethylammonium perchlorate (TEAP) was recrystallized five times from deionized water. Tetrapropylammonium perchlorate (TPAP) was recrystallized three times from 75% (v/v) acetone/water mixture. Tetrabutylammonium perchlorate (TBAP) was recrystallized three times from ethyl acetate/pentane. All supporting electrolytes were dried for 48 hours at 80°C in vacuum after recrystallization and stored in a desiccator. They were also dried in vacuum at 80°C overnight just prior to use.

In ACN the reference electrode was Ag/Ag^+ , 0.04 M AgClO_4 in the same supporting electrolyte as was in the working electrode compartment. All potentials are reported versus this reference. A Luggin capillary was used to minimize ohmic drop between the reference

and working electrodes. Positive feedback iR compensation was used for scan rates above 100 mV s^{-1} .

The EQCM apparatus has been previously described (14,19). Briefly, the oscillation of a thin disk of quartz sandwiched between two gold electrodes is induced with a broadband oscillator circuit. The frequency of the oscillation, which depends on the mass of the disk, electrode, and any material attached to this electrode, is measured using a commercial frequency counter. The polymer films are deposited onto the gold electrodes, and the measurement of oscillation frequency is made in situ, simultaneously with the electrochemical measurements on the film. In this way, the mass changes which occur during the redox event may be monitored. Most of the considerations which pertain to the quantitative calculation of mass from the oscillation frequency have been discussed (13,14,20). The influence of viscoelasticity of the polymer film will be discussed qualitatively in a later section.

The gold EQCM electrodes were coated with the PDNS by dipping the crystal for 20 minutes into a solution of either 0.05 % or 1.0 % (w/v) of the polymer in DMF. The final film thickness was controlled using either the solution concentration or the dipping time as a variable. For PNS, the solution was always 0.05 % (w/v), and the dipping time was between 7 and 12 minutes, depending on the desired thickness. After dipping, the crystals were removed from the solution, shaken carefully, and set aside for 20 minutes (PDNS) or 5 minutes (PNS). The next stage, an essential one for maximum film stability, consisted of baking the crystals in air in a temperature range of 130-180 °C for times ranging from 30 minutes to one hour. Longer times or higher temperatures gave greater stability of the films in solution.

Neutral alumina (Brockmann activity grade I) was placed directly into the cell to maintain the water content of the supporting electrolyte as low as possible. The alumina was activated in the same way as the molecular sieves. The use of alumina in the cell was essential to the long term chemical stability of the polymers. In its absence, the films degraded relatively rapidly due to reactions of the reduced, radical anion forms of the

polymers with adventitious water (21). The supporting electrolyte solutions were degassed for 30 minutes prior to experimentation with Ar which had been purified by passage through molecular sieves (to remove water, oils, etc.) and then an Oxyclear column (to remove trace O_2). For experiments in which it was necessary to control the temperature, a jacketed cell was used in conjunction with a Neslab RTE-110 constant temperature bath.

The conductance spectra of the quartz crystal/polymer film/solution composite resonators were measured with a Hewlett Packard 4192A low frequency impedance analyzer interfaced to an IBM AT using an IEEE-488 interface. It was possible, using this configuration, to measure the conductance under conditions of potentiostatic control of the cell.

Results and Discussion

Conductance spectra

It is a well known and widely exploited fact that the QCM responds to mass changes by changing its resonant frequency of mechanical oscillation. For very thin, rigid (i.e. perfectly elastic) films the relationship between frequency and mass is given by:

$$\Delta f = - C_f \Delta m \quad (1)$$

in which Δf (in Hz) is the frequency change caused by the mass change Δm (in $\mu g \text{ cm}^{-2}$) and C_f is a constant which depends on the mechanical properties of the crystal and its fundamental resonant frequency (which depends on crystal thickness). In the present case, a 5 MHz crystal was used so $C_f = 56.6 \text{ Hz cm}^2 \mu g^{-1}$. A number of cases have been documented in which thin polymer films have been shown to exhibit rigid layer behavior (2,3,12-14), at least in a certain range of thickness and for certain solution conditions. However, this is not to be generally expected for all systems. Thus, the question of whether or not rigid layer behavior prevails must be addressed for each individual system. This is especially true for thin films of organic polymers (as opposed to the more rigid inorganic "polymers" such as oxides) as these materials are known to frequently exhibit viscoelastic behavior which is frequency dependent (22). Considerations of the mechanical behavior of the system are quite important because the linear relationship between mass and frequency indicated by equation

I holds only for rigid films.

There are several ways to determine whether a system behaves rigidly or viscoelastically either in or out of the supporting electrolyte solution (20). The most straightforward way is to measure the conductance spectrum of the QCM/polymer film composite resonator (23). In this experiment, the QCM crystal is exposed to an alternating applied voltage of a precisely synthesized frequency which is swept through the frequency range of the resonance point for the crystal. The conductance of the crystal (G , in $\Omega^{-1} \text{ cm}^{-1}$ or siemens) is measured as a function of frequency, and, from this, the influence of viscoelasticity in the deposit on the resonant frequency is determined (23). The Q or quality factor of the crystal, which is proportional to the ratio of the resonant frequency f_0 (in Hz) to the width at half height Δf_{fwhh} (in Hz) of the conductance, then gives a measure of the extent to which viscoelasticity in the deposit has broadened the resonance.

The value of Q also changes upon simple immersion of the crystal into a viscous medium (23). To a first approximation, it is reasonable to consider the changes in Q from this source as independent of any caused by deposit viscoelasticity, so that significant changes in Q caused by the deposit are simply superimposed on those from the solution. Thus, to determine if a deposit is causing changes in the Q of a crystal, the influence of the solution must first be determined.

Figure 1 shows the conductance spectra of a PNS film immersed in a 0.13 M solution of TEAP in ACN before any electrochemistry (curve A) and after 76 cyclic voltammetric (CV) scans through the potential region in which reduction to the radical anion occurs (curve B). The value of Δf_{fwhh} for the bare crystal in this medium is 1100 Hz. The value in curve A is also 1060 Hz, essentially equal to that for the bare crystal since the resolution of the frequency in the conductance spectrum is 20 Hz. After one scan Δf_{fwhh} is 1200 Hz. After 11 scans Δf_{fwhh} is 2060 Hz, and after 76 scans (curve B) Δf_{fwhh} is 2200 Hz. That the value of Δf_{fwhh} is the same for the bare crystal and the coated crystal in solution is very good evidence that the film is behaving rigidly, i.e. that it does not cause additional broadening of the conductance curve due to viscous loading by the film itself. In addition, these data show

that Δf_{whh} more than doubles after 76 CV scans through the reduction, indicative of large increases in viscosity of the film caused by the redox cycling. Simultaneously with these changes in Δf_{whh} , the resting frequency (i.e. f_r , the frequency attained at the end of the scan, when the film has been electrolyzed back to its oxidized (neutral) form) decreases by between 20 and 200 Hz (depending on the film thickness and heat treatment), after an initial increase due to loss of some of the deposit during the first few scans (see below).

These observations are consistent with extensive swelling of the film during the CV scans. The decrease in f_r , while not of use in a quantitative sense due to the inapplicability of equation 1 under these conditions, does point toward increasing mass as a function of the number of scans. Also, it is known that swelling by solvent induces increases in viscosity (27) and that such increases in viscosity cause decreases in Q and, therefore, increases in Δf_{whh} (23). Thus, the conductance spectra and changes in f_r seem to allow for the qualitative monitoring of solvent swelling during scanning. Unfortunately, a quantitative treatment relating the viscoelasticity of the film to these changes in Q is not available at this time.

The conclusion to be drawn from these data is that equation 1 is not valid for this system, so that the mass changes which occur during the redox event for this film cannot be calculated exactly. However, qualitative information can still be inferred from the observed frequency changes, as will be seen below.

For PDNS, the changes in Δf_{whh} as a function of number of scans through the reduction process are shown in Table 1. Again, it is seen that the Δf_{whh} for the bare crystal in solution matches that for the coated crystal in solution prior to any electrochemical cycling. Thus, the film starts as a rigid film. Even after 30 scans the value of Δf_{whh} has increased only by ca. 6 %, indicative of some swelling, but of a much smaller magnitude. Thus, even though the amount by which Δf_{whh} (or Q) can change before equation 1 becomes invalid is not known at this time, it seems reasonable that changes of this order might not preclude its use.

EQCM/CV experiments

Poly(nitrostyrene). Figure 2 shows plots of current and Δf versus potential for PNS for CV scans into the region for reduction of the pendent nitrophenyl groups to their radical anion states. The CV wave has the characteristics of a simple, one electron, chemically reversible process. As has been previously pointed out by others (15,16,25,26), the wave is rather broad, perhaps indicative of interactions between the pendent redox groups (27) or a distribution of redox potentials due to microheterogeneity within the film (28). The dashed CV (curve A) shows the first scan for the film, and the solid CV (curve B) shows the second scan. The first scan exhibits a diffusion-like response with a rather small peak current, while the second scan resembles more a thin-layer response and has a peak current significantly larger than that of the first scan. The EQCM frequency response for the first scan (curve C, Δf versus E) shows extremely large frequency increases, qualitatively indicative of mass loss, during the reductive branch and the first part of the oxidative branch of the scan. After the anodic wave has been traversed on the return (positive) scan, the frequency begins decreasing again, probably due to regain of some of the mass lost during the reduction.

That the CV during the first scan seems much more diffusion-like than the second is consistent with a rather compact film which has not yet been "broken-in" prior to electrochemical cycling. These break-in effects have been observed by others before, and do, in fact, seem to be related to solvent swelling (29). The smallness of the peak current in this scan with respect to that in the second scan probably indicates that the rate of charge propagation through the film is faster in the second scan than in the first. This would indicate a correlation of increased swelling with increased charge transport rates, a conclusion which agrees with earlier proposals for other systems (29).

The Δf versus E curve seems to show the loss of considerable material on the first scan. This is probably due to dissolution or delamination of the film following its reduction, perhaps due to loss of low molecular weight material. The shape of the Δf curve when the frequency begins to decrease on the return scan has the characteristics of a diffusion-like ($t^{1/2}$) response which may indicate the redeposition of some of the dissolved polymer. These features are almost identical to those observed for thick films of poly(vinylferrocene) in Cl^-

containing aqueous media, in which film dissolution has been previously observed (14).

Figure 3 shows the CV and EQCM data representative of the behavior of PNS in later scans. The dashed curve in plate A is the CV, which shows a large wave at -1.55 V and some evidence of a small prewave at -1.35 V. This prewave is probably caused by a small amount of dinitrated rings in this sample of PNS (see below). The solid curve is the derivative of the frequency change with respect to potential (df/dE). The quantitative connection between df/dE and current has been discussed previously (30). Briefly, since the current is the instantaneous rate of electron (or hole) consumption and df/dE gives the instantaneous rate of change of mass, the two curves may be compared directly if an assumption is made regarding the mass transferred per electron. For the sake of comparison, it is assumed in the present case that the cation (TPA^+) is the species undergoing transport, so that the molar mass of the cation is used in the calculation of df/dE from Δf versus E . Thus, the extent to which there is a discrepancy between the current (i) and df/dE curves serves as an indication of transport behavior which is not dictated solely by permselective, unidirectional transport of this species. Specifically, if either anion or solvent net transport contribute to the observed mass change, then there will be discrepancy between i and df/dE (except for cases of fortuitous cancellation).

Plate A clearly shows that the overall direction of the mass change seems to be that expected for permselective transport (i.e. mass gain due to cation insertion during reduction and mass loss due to cation expulsion during oxidation), but that the magnitude of the mass changes are larger than would be predicted based solely on cation transport. A likely (but certainly not the only) explanation for this observation is that some solvent transport occurs in the same direction as the cation transport, so that the net mass change also has a contribution from the mass of this solvent. This interpretation of the frequency changes during scanning would seem to be in agreement with the observed increase in Δf_{fwhh} as a function of the number of scans, since both effects can almost certainly be attributed to increased solvent content within the film.

The peak in the df/dE curve is nearly 75 mV positive of the peak current (i_p). This

could be caused by the predominance of swelling early in the reduction, as opposed to the maintenance of a constant ratio of cation to solvent transport throughout the scan. An alternative explanation is that the largest changes in viscoelasticity for the system are early in the reduction, and that these changes cause the frequency to decrease nonlinearly with respect to the extent of electrolysis of the film. However, if the viscoelastic changes are caused primarily by changes in the solvent content of the film, then both explanations lead to the same conclusion, namely that solvent enters the film early during reduction and leaves late during oxidation, early and late being measured with respect to the consumption of charge. The relative positions of the peaks in the dsf/dE and i curves depend on scan rate, indicating that these are not equilibrium responses. However, quite similar behavior is seen for TEA^+ , TPA^+ , and TBA^+ cations when compared at the same scan rate.

Plate B in Figure 3 shows the behavior of the film in the seventh scan. The dsf/dE curve is significantly smaller than the current. Also, the peak in dsf/dE is still positive of the current peak, but by a slightly smaller amount. The value of f_T just before the scan was about 150 Hz below its starting value, and Δf_{fwhh} had increased by ca. 30 % compared to its value before any scanning had taken place. These changes in f_T and Δf_{fwhh} probably result from swelling of the film, as discussed above. If this is true, then there should exist within the film a significant reservoir of anions (either dissociated from or aggregated with their counterions from the supporting electrolyte, depending on the effective dielectric constant of the medium). It is worth noting that this quantity of sorbed counterions can be very much in excess of the number of fixed charges on the polymer if the extent of swelling is large. This situation allows for the possibility of mixed transport (i.e. simultaneous anion and cation transport), so that the net mass change may cause dsf/dE to be larger than, smaller than, or even of opposite sign to the current. As has been recently pointed out (3), the attainment of thermodynamic equilibrium dictates this net mass change in a way which is not readily predictable *a priori*, primarily due to uncertainties as to the dependence of activity coefficients on concentration. Given a situation of this type, mass transport is not unambiguously elucidated by the EQCM data. All that can be said is that there appears to be

net transport out of the film during the reduction, and into the film during oxidation. In fact, it cannot even be asserted with any certainty that mixed cation and anion transport occurs (one possible way to account for the difference between da/dE and i), because the amount of solvent transport has not been determined for this case. However, one thing that does seem clear is that prolonged cycling over the reduction wave for the pendent nitrophenyl moieties leads to significant swelling of the film, with this swelling leading to a situation which is not well described by a model based solely on permselectivity.

As was mentioned above, the stability toward solvent swelling of the PNS films is markedly influenced by the details of the heat treatment during film preparation. Figure 4 shows the CV and af versus E curves for a film which was heat treated for one hour at 180 °C (type II films), as opposed to the 130 °C, 30 minute treatment for the films described above (type I films). Again, the prewave from the small fraction of dinitrobenzene rings is seen. The overall shape of the wave for the mononitrated rings at -1.55 V is quite similar to those shown above. However, the af versus E data are distinctly different. There is less hysteresis in this curve than for type I films. Also, the frequency essentially reattains the value it had prior to the scan, in contrast to the behavior of type I films (recall that f_r continuously decreases with scanning for type I films which was attributed to retention of monotonically increasing amounts of solvent). However, the magnitude of the frequency change for these films still seems to be indicative of a relatively large degree of solvent incorporation coincident with the cation insertion process. Thus, these data support the notion that significant solvent swelling does occur for type II films, but that it is more reversible than for type I films. This behavior would be consistent with the type II films having a larger number of crosslinks which would act to inhibit the irreversible swelling which occurs for the type I films. Such crosslinks could be of chemical origin (i.e. some type of thermally induced covalent bond formation between chains) or of physical origin (i.e. strong physical attractions between chains such as might occur in crystalline (as opposed to amorphous) regions of the films). Attempts to detect such phenomena using *ex situ* FTIR measurements have so far been unsuccessful.

At higher scan rates, the hysteresis of the Δf versus E curves becomes much more pronounced, even while the CV curves remain quite symmetric, as shown in Figure 5. The peak current is nearly 10x larger than that in Figure 4, and the charge is nearly identical, as expected for a film exhibiting thin layer behavior. However, the frequency decrease with reduction is much smaller than that in Figure 4. In fact, as scan rate is increased, the frequency decrease during reduction approaches a limiting value (finally reached at ca. 600 mV s^{-1}), the magnitude of which indicates that essentially no solvent transport occurs during the cation insertion for reduction. In other words, the mass change during reduction is consistent with the insertion of one cation per electron injected into the film, and no accompanying solvent. Experiments with TPA^+ and TEA^+ give analogous results.

On the return scan for all type II systems at high scan rates, the time required for the frequency to reattain its original value is much longer than the time for passage of the electrochemical charge, as shown in Figure 5. This must result from a decoupling of the transport processes responsible for the maintenance of electroneutrality and for the attainment of thermodynamic equilibrium. Thus, during the oxidative scan, there must be simultaneous anion insertion and cation expulsion to maintain electroneutrality, with these occurring on the timescale of the passage of the electrochemical charge (i.e. they must be essentially completed at -1.40 V). In contrast, the mass transport to achieve thermodynamic equilibrium occurs predominantly after the passage of the charge. This may involve some solvent transport and a change in the relative populations of anions and cations within the film. While this picture of the time evolution of the mass transport processes during redox cycling for these films is rather tentative, it does make clear that the mass transport processes which are induced by electrochemical cycling need not occur simultaneously with the passage of the charge. They also show that transient, nonequilibrium states can occur due to the requirement of electroneutrality, and that these nonequilibrium states can evolve to the equilibrium condition on a timescale much longer than that of the charge consumption. The implication is that the conditions at equilibrium need not dictate the ultimate charge propagation (switching) rates for thin films of either redox or conducting polymers if the

needs of electroneutrality can be met by transient, nonequilibrium states.

Partially dinitrated poly(styrene). Figure 6 shows the behavior observed for PDNS for the 1st, 5th, and 44th scans. The voltammetry of the 1st and 5th scans shows the presence of two waves. The first (at ca. -1.35 V) is attributed to the reduction of the dinitrated phenyl groups (31). The second (at ca. -1.60 V) is from the reduction of the mononitrated phenyl groups (16). These assignments are supported by the observation of these redox processes for authentic samples of mono- and dinitrotoluene (32).

The reduction of the dinitrated groups is by far larger than that for the mononitrated groups early in the lifetime of the film, but disappears entirely after 10-15 scans, depending on film thickness. This may be due to a combination of loss of much of the film material during the first few scans (as judged by the large, irreversible increases in frequency coincident with reduction in the first few scans) and a scavenging effect performed by the dinitrated groups. Since these nitro radical anions are known to be exceedingly sensitive to the presence of water, it seems reasonable to suggest that the first groups to be reduced will act to scavenge adventitious water from within the film, and be irreversibly reduced in the process. These reduction processes lead to products such as azo compounds (15,21,24) which can act as crosslinks within the film. In fact, the PDNS films are far more stable than the type I PNS films (see below), perhaps due in part to such crosslinks. However, if this is true, it is not clear why the same effect is not observed for the mononitrated films.

The EQCM frequency data show that, for the 5th and 44th scans, there is mass gain on reduction and mass loss on oxidation. Reduction of the dinitrated groups shows essentially the same mass gain and loss characteristics as the mononitrated groups.

Figure 7 shows $\Delta f/dE$ (solid) and i (dashed) versus E for the 2nd scan of a PDNS film. Keeping in mind that for PDNS the rigidity of the film (as judged by the relatively constant value of Δf_{fwhh} with scanning) allows for the quantitative calculation of mass from Δf , it is clear that reduction of this film causes a net mass increase significantly larger than would be explained on the basis of permselective cation transport to maintain electroneutrality. It seems likely that considerable transport of solvent occurs simultaneously

and in the same direction as cation transport, although other situations involving mixed transport cannot be ruled out. If this is the case, the data also indicate that most of the swelling occurs during the first reduction process. The lower curve in the figure shows the plot of Δf versus E for this scan. The important point to note here is that the frequency does not return to its original value. Rather, it remains at a lower value after the scan. Waiting at potentials at which the film is in its neutral form (e.g. 0.0 V) for several minutes allows for the frequency to increase somewhat, but it never increases completely to reattain the value before the scan. This continuous decrease in frequency occurs for every scan (in ACN), with the swelling becoming so extensive as the number of scans increases (see below) that the film eventually begins to dissolve away from the surface, as judged by mass loss and loss of charge for the redox process. However, this swelling/dissolution process is much slower for PDNS than for PNS (in spite of the much larger molecular weight of PNS), probably due to the chemical crosslinks in PDNS caused by the presence of azo coupling (15,21,24).

By monitoring f_r versus the number of scans, it is possible to obtain a measure of how the extent of swelling changes with scanning. It is worth pointing out here that such experiments must be done under conditions of rigorous temperature control to obviate the possible influence of changes in viscosity of the supporting electrolyte solution on the resonant frequency of the immersed crystal (20,33). Figure 8 shows a plot of f_r versus number of scans for a PDNS film. In this case, the value of f_r was measured immediately after the scan. The film mass is seen to increase significantly with scanning, almost certainly as a consequence of swelling.

This behavior can be correlated with the transport behavior. Table 2 shows the ratio of the net mass gain during the scan (not to be confused with f_r) to the charge consumed in the redox process as a function of increasing scan number. These data indicate the mass change per electron decreases dramatically as the number of scans increases. It is proposed that this behavior is due to the extensive swelling which occurs with scanning. Thus, the increased swelling leads to sorption of both solvent and supporting electrolyte, so that the transport processes which serve both to maintain electroneutrality and to maintain

thermodynamic equilibrium across the film/solution interface probably evolve from being mostly permselective (with some concomitant solvent transport) to a situation with mixed anion and cation transport and perhaps solvent transport. Unfortunately, due to the complexity of the situation, the picture must remain a qualitative one, given the available data.

Conclusions

The behavior of PNS and PDNS is shown to be a strong function of the extent of solvent swelling of the film. For PNS, the solvent swelling is quite extensive, and the film stability seems to suffer as a consequence of this. This tendency can be countered somewhat by more rigorous thermal pretreatments, the exact function of which is not yet known. This solvent swelling does not have a dramatic influence on the morphology of the electrochemical response, other than to cause a continuous decrease in the charge. An exception to this is the behavior during the first few scans in which the films are "broken-in" (i.e. swollen by solvent due to the forced transport of ionic species during the redox cycling) to facilitate faster charge propagation.

The kinetic experiments on the type II PNS films have shown that the attainment of electroneutrality and thermodynamic equilibrium need not be coupled. This is an important result, in that it suggests that transient, nonequilibrium states may be manipulated to achieve rapid switching (i.e. fast charge propagation rates), and that in some cases this may be done independently of the transport processes which occur to attain thermodynamic equilibrium. We have observed this type of behavior in other thin film systems and will report on it in a future publication.

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TABLE 1

Δf_{fwhh} VALUES FOR
PARTIALLY DINITRATED POLY(STYRENE)
DURING ELECTROCHEMISTRY.

NUMBER OF SCAN	FULL WIDTH AT HALF HEIGHT, Δf_{fwhh}
0	1370 Hz
1	1406 Hz
7	1426 Hz
30	1454 Hz

Coverage: 9.5 nF/cm^2 . Supporting electrolyte: 0.18 M TBAP .

Scan Rate: 50 mV/s . Δf_{fwhh} for the uncoated electrode immersed
in the same solution: 1350 Hz .

TABLE 2
RATIO OF THE NET MASS GAIN TO CHARGE

<u>FIRST WAVE</u>			
Scan number	coverage	mass/charge (gr/mole)	excess [*]
2	8	705.1	11
3	7	504.8	6
5	6	478.0	5.7
7	5	415.1	4
13	4	185.5	<1

<u>SECOND WAVE</u>			
3	1.6	687.5	11
5	1.6	466.4	6
7	1.5	433.0	5
13	1.3	261.5	3

Scan rate: 50 mV/s. Supporting electrolyte: 0.15M TBAP. Coverage:
(first wave) $\times 10^{-10}$ mole/cm²; (second wave) $\times 10^{-9}$ mole/cm².

***Excess:** This corresponds to the number of solvent inserted
per cation during electrochemistry of the film.
TBA⁺(242.48 gr/mol); acetonitrile(41 gr/mol).

FIGURE CAPTIONS

- 1- Conductance Spectrum. Poly-p-nitrostyrene coating (Heated at 170°C, 50 minutes). Coverage: 8.3nF/cm². Supporting electrolyte solution: 0.13M TEAP. A- Before electrochemistry. Δf_{fwhh} : 1060 Hz. B- After 76 potential scans Δf_{fwhh} : 2200 Hz.
- 2- Poly-p-nitrostyrene. Coverage: 10×10^{-8} mole/cm². CV/QCM steady state scan from -0.4 V to -1.85 V. Scan rate: 50 mV/s. Supporting electrolyte solution: 0.13M TEAP. A- Dashed voltammogram, first scan. B- Solid voltammogram, second scan. C- Frequency response for the first scan.
- 3- Poly-p-nitrostyrene. CV/QCM steady state scan from -0.4 V to -1.85 V. Supporting electrolyte solution: 0.13M TPAP. Scan rate: 50 mV/s. A- Second scan. Dashed voltammogram: actual current. Solid corresponds to $d\Delta f/dE$ B- Seventh scan. Dashed voltammogram: actual current. Solid is $d\Delta f/dE$
- 4- Poly-p-nitrostyrene. C:/QCM steady state scan from -0.6V to -1.85V. Supporting electrolyte solution: 0.15M TEAP. Scan rate: 50 mV/s.
- 5- Poly-p-nitrostyrene. CV/QCM steady state scan from -0.6V to -1.85V. Supporting electrolyte: 0.15M TPAP. Scan rate: 600 mV/s.
- 6- Partially dinitrated poly(styrene). CV/QCM steady state scans. Δf corresponds to the frequency change in Hz. Supporting electrolyte: 0.2M TPAP. Scan rate: 50 mV/s.
- 7- Partially dinitrated poly(styrene). Supporting electrolyte: 0.13M TPAP. Scan rate: 50 mV/s. a- Dashed voltammogram is the actual current. b- Solid one corresponds to $d\Delta f/dE$. Δf_r : change in the resting frequency, f_r .
- 8- Partially dinitrated poly(styrene). Supporting electrolyte: 0.15M TEAP. Scan rate in all scans: 50 mV/s.















